

has tank instead of river water as an alternative to the filtered supply, on the other hand, has a spleen-rate of 14·8, which is almost the same figure as that of Maniktolla, with a similar water-supply. Further, those Wards which are situated immediately on the river bank, but do not possess a filtered water-supply, and consequently get their supply mainly from the river, and to a less extent from tanks, have a rate intermediate between those with filtered water and the inland ones which are dependant entirely on tank water. In short, all the Ward variations in the spleen-rate of the whole area can be explained on the ground of their varying water-supplies in a manner which no other explanation will approach in completeness, so that it is impossible to come to any other conclusion than that the above is the true explanation of the facts recorded. Whether the *Anopheles* mosquitos play a part by taking the malarial parasite back to the tanks from their human hosts or not must be left to be determined by future experiments, but that a good water-supply is an important prophylactic measure in the lessening the prevalence of malaria must I think be admitted, and can be safely acted on.

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XVIII.—I. *Further Researches on Mercurous Nitrite and its Derivatives.*

II. *On Mercurous Iodide and a new Method of its Preparation.*—By

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- II. Mercurous Iodide: a new Method of its Preparation.

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(1)

PREPARATION OF MERCUROUS NITRITE ON A LARGE SCALE.

As the investigations I am about to describe involve the use of comparatively large quantities of mercurous nitrite at a time I shall

begin with describing a method of preparing the salt, which has been found to be more economical and far less troublesome than the usual method.

A tall beaker is taken containing nitric acid (sp. gr. 1.041) diluted in the proportion of 1 : 4 with water; mercury is now poured in, care being taken not to fully cover the bottom but to leave an annular or horse-shoe-shaped space. The crystals which are formed on the convex surface of the mercury are continually pushed aside into the empty space by the evolution of gases during the initial stages of the reaction. On standing overnight, however, a crust of the nitrite is formed on the surface of the metal, which acts as a protective layer, thereby hindering further action.

All that is now necessary to do is to incline the beaker gently, when the deposit of the salt slips off into the empty space as explained before, leaving a fresh surface of mercury exposed. This may be repeated 4 or 5 times in the course of the day. Instead of inclining the beaker, the layer of crystals may be carefully scraped off the surface with a glass rod. The process may be allowed to go on for a week, resulting in the continuous growth and accumulation of the salt; the reaction may be started simultaneously in about half a dozen beakers arranged in a row, so as to secure a copious supply.

In the previous papers\* it was recommended that each time a layer of crystals is formed, the mother liquor together with the mercury should be decanted off into another beaker. This is a wasteful method, for as soon as the super-incumbent liquid is removed, torrents of red fumes appear on the surface of the mercury. These red fumes are caused by the combination of nitric oxide with the oxygen of the air. It is the nitric oxide that evidently gives rise to the formation of the nitrite, and its loss has to be guarded against.

(2)

PREPARATION OF CHEMICALLY PURE MERCUROUS NITRITE.

The mercurous nitrite prepared as above will answer well enough for ordinary purposes. It generally contains, however, impurities, chiefly in two shapes. First, the crystalline mass encloses minute globules of mercury which cannot be entirely detached. Secondly, as the salt has to be dried on the porous tile, a portion of the heavy mother liquor consisting of mercurous *nitrate* dries up along with it. When it is desirable to obtain the salt in a state of absolute purity, it is mixed with a sufficiently large quantity of water and heated to boiling point for some

\* For literature on the subject, see *Journal, Asiatic Society*, 1896, Pt. ii, p. 1, and *Transactions, Chem. Soc.* for 1897, p. 338.

time. Treated in this way about 18 p.c. of the nitrite undergoes dissociation as already pointed out; thus:



While by far the larger proportion of it dissolves *as such*; the saturated solution while still hot is rapidly passed through a "ribbed" filter paper, and the filtrate briskly stirred with a rod. In this way a fine, mealy, crystalline deposit is obtained, which is dried on a porous tile and preserved *inside a dessicator*. The presence of even a trace of atmospheric moisture brings about slow decomposition evolving nitrous fumes. As a test case it may be mentioned that 0.54 g. of the pure salt was placed on the scale pan for three hours, and it lost 5 mgs. during that time.

### (3)

#### INTERACTION OF MERCUROUS NITRITE AND ETHYL IODIDE.

##### *Preliminary.*

About four years ago while describing mercurous nitrite and its general properties, which were found to bear a remarkable analogy to those of silver nitrite, the author expressed a hope that this new compound would yield nitro ethane by interaction with ethyl iodide.

Since then it has been qualitatively shown that the reaction gives simultaneously both nitro ethane and its isomer, ethyl nitrite.\* The present investigation embodies a fuller and more systematic study of this reaction.

##### *Experimental.*

The general method first described by V. Meyer and O. Stüber has been in the main followed.† I shall therefore confine myself to such details only as have a direct bearing on the subject in hand.

Exp. I. 120 g. of mercurous nitrite and 69 g. of ethyl iodide were digested together over a water bath in a round-bottomed flask to which was attached a tubulated funnel and a reflex condenser. The digestion was continued so long as ethyl nitrite was evolved. It is necessary to note here that as soon as ethyl iodide is poured on silver nitrite, an energetic action at once sets in, but when mercurous nitrite is added to the alkyl iodide there is scarcely any perceptible evolution of heat, and the reaction only begins after digestion has proceeded for some time. The open

\* Proc. Chem. Soc. 1896, p. 218.

† Ber. Deut. Chem. Ges., V, pp. 399, 514.

end of the condenser was connected with two tall cylinders (See Fig.)

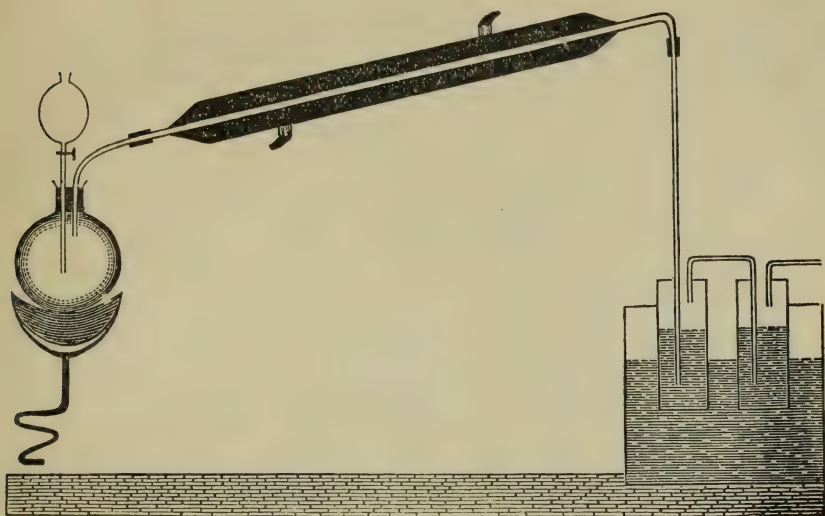


Fig. shewing the formation of Ethyl Nitrite and its absorption by Alcohol.

containing a measured volume of alcohol for the absorption of ethyl nitrite. These cylinders were again kept immersed in ice-cooled water of an average temperature of  $10^{\circ}\text{C}$ ., that of the Laboratory varying from  $23^{\circ}$  to  $25^{\circ}\text{C}$ . In this manner a concentrated solution of what is called in the Pharmacopœia *Spiritus Ætheris Nitrosi*, was obtained, the strength of which was determined by Allen's method.\* The yield of ethyl nitrite was found to be 5.1 g.

Exp. II. 94 g. of mercurous nitrite and 35 gms. of ethyl iodide were digested as above. The yield of ethyl nitrite was 3.1 g.

Exp. III. In this case 138 g. of mercurous nitrite were digested with 54 g. of ethyl iodide, yielding 5.2 g. of ethyl nitrite.

It will thus be seen that the yield of ethyl nitrite is only a fraction of what is demanded by theory. This is partly due to the reaction being completed only during subsequent digestion on the oil bath, but chiefly to the fact that when once a certain amount of mercurous iodide has been superficially formed, a large proportion of the nitrite aggregates into hard lumps into which the ethyl iodide can only slowly and with difficulty penetrate.

\* *Pharmaceutical Journal*, 3rd Series, Vol. XV, p. 673.

This is also the case with silver nitrite, though not in so marked a degree.\*

Exp. IV. This was a control experiment in which silver nitrite was digested with ethyl iodide: 90 g. of the silver salt were treated with 88 g. of the alkyl haloid. The yield of ethyl nitrite was 4.2 g.

#### NITRO ETHANE.

After the evolution of ethyl nitrite had ceased, the contents of the flask were subjected to distillation, first over a water bath, and afterwards over an oil bath. The distillates were caught separately.

It was invariably found that during distillation over an oil bath, the receiver was filled with nitrous fumes, a part of which was absorbed by the distillate, imparting to it a bluish tinge. As there was not the slightest trace of yellow colour either in the flask or in the condenser itself, it was suspected that *nitric oxide* was evolved by the slow and gradual decomposition of a portion of mercurous nitrite, which combined with the oxygen of the air in the receiver. The suspicion was confirmed. The presence of the nitrous fumes is highly objectionable, as the crude nitro ethane so obstinately holds them in solution that they cannot be got rid of during fractionation. Distillation in a slow current of carbon dioxide was therefore resorted to for excluding air. In the control experiment with silver nitrite (See *ante*, Exp. IV.) nitrous fumes, though in a far lesser degree, were also noticed in the receiver.†

After the distillation was over, the compact mass of mercurous iodide and nitrite were removed from the flask, well powdered in a mortar, and once more treated with the fraction below 100°, when a further quantity of crude nitro ethane was obtained.

A fair idea of the yield of nitro ethane may be had from the details of one among several experiments. 190 g. of mercurous nitrite and 95 g. of ethyl iodide yielded a distillate of 7 g. between 100°–108°, of 3¼ g. between 108°–110°, and of 4 g. between 111°–114°.

The fraction which came off between 113°·5'–114° (uncorrected) was practically pure nitro ethane. It was treated with an alcoholic solution of caustic soda as recommended by Nef. (*Annalen*: 280, p. 267). The

\* "Es gelang uns unter keinen Umständen das ganze Jodäthyl in die Reaction zu verwickeln, sondern stets war das bei der Rectification zuerst übergehende Produkt stark jodhaltig. Wir haben auf jede weise versucht, das Jodäthyl vollständig anzubenten, doch immer vergeblich." (*Loc. cit.*, p. 402.)

† The behaviour of Mercurous Nitrite in this respect also resembles that of Silver Nitrite. Cf. Divers and Schimidzu "Action of heat upon Silver Nitrite, air being excluded"—(*Trans. Chem. Soc. Journ.*, 47, 634), where it is shown that nitric oxide is one of the products of decomposition.

precipitate of sodium nitro-ethane was washed with absolute alcohol. In this manner 2.5 g. of nitro-ethane yielded 2.1 g. of the sodium compound.

It responded to all the characteristic reactions: its aqueous solution turned blood-red with ferric chloride and green with copper sulphate. A concentrated solution of it gave with corrosive sublimate solution a white, mealy, crystalline precipitate. The sodium salt which is extremely hygroscopic exploded with a loud detonation when heated in a narrow test tube. An estimation of sodium is given below.

|             |                                      |                                         |
|-------------|--------------------------------------|-----------------------------------------|
|             | 0.2416 g. gave                       | 0.1795 g. of $\text{Na}_2\text{SO}_4$ . |
|             | Calc. for                            | Found.                                  |
| $\text{Na}$ | $\text{Na C}_2\text{H}_4\text{NO}_2$ | 24.06.                                  |
|             | 23, 60                               |                                         |

From the above investigations it would appear that by the action of mercurous nitrite on ethyl iodide about equal quantities of nitro ethane and its isomer ethyl nitrite are formed. The yield is, however, somewhat poorer than with silver nitrite, owing to the formation of very compact, hard lumps of mercurous iodide, which interferes with the reaction being completed.

## (4)

INTERACTION OF MERCUROUS AND MERCURIC NITRITES WITH THE NITRITES  
OF SILVER AND SODIUM.

## 1.

*Mercuric Nitrite and Sodium Nitrite.*

To the neutral solution of mercurous and mercuric nitrites (the products of dissociation of mercurous nitrite: Journ. Chem. Soc. Trans. 1897, p. 340) is added sodium chloride to remove mercurous mercury. The filtrate which now contains mercuric nitrite and a small quantity of sodium chloride if it was added in excess, as well as *sodium nitrite*, is allowed to evaporate spontaneously. In course of time an orange, crystalline deposit is formed, and this is followed by the appearance of shining iodine-like dark scales; and last of all we obtain a yield of rhombohedral crystals of *sodium nitrate*. Sometimes the orange-red and black compounds are not obtained, but instead we get only sodium nitrate, sometimes again the three compounds are obtained in regular succession, though one kind may predominate over the others.

During the last three years I have repeated the experiments several times, but I have not been able so to control them as to ensure the formation of one variety only to the exclusion of the others.

If there be no sodium chloride present in the mercuric solution, the red and black deposits are not formed, for, as will be seen below,

they are oxychlorides of mercury and the presence of sodium chloride is a *sine quâ non* for their formation, and the only yield is one of sodium nitrate. But this last compound has sometimes been observed as the sole product without the formation of the former, even in presence of an excess of sodium chloride. The reaction goes on very slowly, and it takes a month and upwards to complete it.

Analysis and general properties of the red and iodine-like lustrous scales:—

- (1) 0.3505 g. gave 0.3485 HgS.  
 (2) 0.465 „ „ 0.455 „  
 (3) 0.5086 „ „ 0.2034 AgCl.  
 (4) 0.6166 „ „ 21.1 c.c. moist O at 31° C. and 752 mm. pressure.

|                  | Theory for                 | Theory for                                                 | Found |       |
|------------------|----------------------------|------------------------------------------------------------|-------|-------|
|                  | Hg Cl <sub>2</sub> . 2 HgO | Hg Cl <sub>2</sub> . 2 HgO. $\frac{1}{2}$ H <sub>2</sub> O | i     | ii    |
| Hg               | 85.35                      | 84.27                                                      | 84.45 | 84.34 |
| Cl               | 10.10                      | 9.97                                                       | 9.90  |       |
| O                | 4.55                       | 4.50                                                       | 4.17  |       |
| H <sub>2</sub> O |                            | 1.26                                                       |       |       |
|                  | 100.00                     | 100.00                                                     |       |       |

The analyses recorded above are of distinct preparations, and they conform to the formula HgCl<sub>2</sub>. 2 HgO.  $\frac{1}{2}$  H<sub>2</sub>O.

These salts do not lose in weight when kept in a dessicator over strong sulphuric acid or placed in a steam chamber at 100° C. When heated in a bulb-tube a deposit of moisture is invariably noticed, and a sublimate of mercurous and mercuric chloride obtained, with a residue of orange-yellow oxide. Treated with caustic soda solution, the dark variety changes to orange-yellow.

Millon, and more recently Thummel (Archiv. Pharm. § [3], 27, 589-605) have exhaustively studied the oxychlorides of mercury, and have described several of them. These were obtained, however, by adding together solutions of mercuric chloride and hydrogen potassium carbonate under varying conditions. Volhard got shining dark crystals by the action of sodium acetate upon corrosive sublimate solution (Annalen : 255, p. 252); whilst Haack obtained a reddish-brown crystalline deposit by treating mercuric chloride with phosphate of sodium (*ibid.* 262, 189), all of the formula HgCl<sub>2</sub>. 2 HgO. The red and black shining compounds, the subject of the present paper, agree in general

§ The Original Memoir is not available here. I am quoting from Watt's Dict. of Chem., New Ed. See also Abs. Chem. Soc. Journ., Vol. LVI, 1050.

properties with those obtained by the above chemists; but the *hydrated* modifications I do not find mentioned anywhere.

## I.

*Mercurous Nitrite and Silver Nitrite.*

A. Concentrated solutions of mercurous nitrite and silver nitrite.

As both mercurous nitrite and silver nitrite are very sparingly soluble in cold water, the solutions used were always kept at about 100° C.

*Method of experiment*:—To the hot or boiling solution of mercurous nitrite containing necessarily mercuric nitrite was added the solution of silver nitrite. No effervescence due to the evolution of gases was noticed, and the liquid which at once became cloudy on account of the separation of metallic mercury, was allowed to stand over night. Next day a perfectly clear solution was obtained, with a deposit of mercury and silver in successive layers at the bottom of the vessel,—the lower one of dirty grey mercury, and the upper one of an arborescent and filamentous growth of shining minute crystals of silver. These metals were estimated in the usual way. The strength of the filtrate was determined by finding out the weights of the *ous* and *ic* mercury as well as that of silver in solution. Control analyses were also simultaneously made to ascertain the original strengths of the mercury and silver nitrite solutions under exactly similar conditions of temperature. For details see Table of Analyses.

In order to estimate the total amount of nitrogen and the transformation, if any, of the nitrite into nitrate, or any other compound of nitrogen, the following method of analysis as exemplified in Exp. I was adopted.

50 c.c. of mercurous and mercuric nitrite solution were boiled for a few minutes with an excess of caustic soda; 25 c.c. of silver nitrite solution were also similarly treated. The filtrates from the mercury and silver precipitates, containing nitrogen in the shape of nitrite of sodium, were now added together and made up to a given volume. After the interaction of mercurous and silver nitrite solution, an aliquot portion of it was boiled with the alkali, and the filtrate set aside as above. The nitrogen in both the cases was estimated by the Crum-Frankland process, as also by the *Urea* method as worked out by Percy Frankland. As a further check a few c.c.'s were in certain instances evaporated to dryness in a porcelain boat and the nitrogen determined by Dumas' method. It is remarkable that the sum total of nitrogen as found by all these different methods was exactly the same, proving that *not only was there no loss of nitrogen during the reaction but that it remained ill*



along in the shape of the nitrites of the respective metals, in other words, there was no change in the radical  $\text{NO}_2$ .

B. Dilute solutions of silver and mercurous nitrite, (*vide* Exp. 5 and 6 in the Table of Results of Analyses).

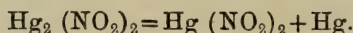
It is worthy of note that under such conditions of dilution no silver was precipitated.

### C. Mercurous Nitrite and Sodium Nitrite.

In this case also the total amount of nitrogen remained constant, and in the shape of nitrites, the only difference being that the mercurous nitrite was completely transformed into mercuric nitrite with precipitation of mercury. In Exp. 7 a 6% solution of sodium nitrite was used. Sodium nitrite was, however, found to have scarcely any action on very dilute solutions of mercurous nitrite.

### DISCUSSION OF RESULTS.

It is not easy to enter into the mechanism of the reaction of mercurous and silver nitrites, when it is remembered that there is no change in the radical  $\text{NO}_2$ . Mercurous nitrite, it is true, has already been shown to undergo partial dissociation according to the equation,



when in solution; but the reaction, we are at present studying, can scarcely be brought under the same category. At the same time, it must be admitted that, if we were to regard for a moment a molecule of silver nitrite playing the role of a molecule of mercurous nitrite, all the equations under A. could be established on a common basis.

For instance in Exp. 1,  $3 \text{HgNO}_2 + \text{AgNO}_2$  may be regarded as equivalent to  $4 \text{HgNO}_2$ , *i.e.*,  $2 \text{Hg}_2(\text{NO}_2)_2$  which may be expected to dissociate as follows:—

$2 \text{Hg}_2(\text{NO}_2)_2 = 2 \text{Hg}(\text{NO}_2)_2 + 2 \text{Hg}$  [or  $\text{Hg} + \text{Ag}$ ]. In Exp. 3,  $7 \text{HgNO}_2 + 3 \text{AgNO}_2$  would similarly be equivalent to  $10 \text{HgNO}_2$  *i.e.*,  $5 \text{Hg}_2(\text{NO}_2)_2$  which would dissociate thus:  $5 \text{Hg}_2(\text{NO}_2)_2 = 5 \text{Hg}(\text{NO}_2)_2 + 5 \text{Hg}$  [or  $2 \text{Hg} + 3 \text{Ag}$ ], with this difference, that in place of  $2 \text{Hg}$  we get  $\text{Hg} + \text{Ag}$ , and in that of  $5 \text{Hg}$  we get  $2 \text{Hg} + 3 \text{Ag}$ . In Exp. 5 and 6 bracketted together under B., where dilute solutions of both the nitrites were used, and where there was no precipitate of metallic silver, the nitrite of silver apparently seems to take no part. The same remarks would also apply to Exp. 7 and 8 (*vide* Table of Analyses), where sodium nitrite also appear to act *catalytically*, an expression conveniently used to cover ignorance. The true explanation of the reaction has yet to be found out, and with this view, it is intended to take up another series of experiments under various degrees of dilution of the nitrites.

Table of Results of Analyses.

| No of Exp. | A   |        | B     |       | C  |       |
|------------|-----|--------|-------|-------|----|-------|
| (1)        | 50  | 1.074  | 0.863 | 0.620 | 20 | 0.620 |
| (2)        | 50  | 0.685  | 0.676 | 0.486 | 20 | 0.700 |
| (3)        | 25  | 0.173  | 0.188 | 0.382 | 20 | 0.242 |
| (4)        | 100 | 0.564  | 0.569 | 0.454 | 50 | 0.172 |
| (5)        | 100 | 0.3454 | 0.382 | 0.392 | 50 | 0.392 |
| (6)        | 100 | 0.488  | 0.486 | 0.507 | 50 | 0.442 |
| (7)        | 25  | 0.081  | 0.081 | 0.333 | 20 | 0.333 |
| (8)        | 25  | 0.980  | 0.980 | 0.980 | 20 | 0.980 |

| Reaction as Expressed in Formula.                                                                                                                                                                                                                                                                        | Wt. of "free" Silver. | Wt. of Ag in Sol. | Wt. of "free," i. e., pptd. Mercury. | Wt. of "free" Silver. |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|-------------------|--------------------------------------|-----------------------|
| $6 \text{ Hg}^{\text{I}} \text{NO}_2 + 5 \text{ Hg}^{\text{II}} (\text{NO}_2)_2 + 3 \text{ Ag}^{\text{I}}$<br>or $3 \text{ Hg}^{\text{I}} \text{NO}_2 + 2 \text{ Hg}^{\text{II}} (\text{NO}_2)_2 + \text{H}_2$<br>+ $2 \text{ Ag}^{\text{I}}$                                                            | 0.168                 | 1.205             | 0.564                                | 0.168                 |
| $5 \text{ Hg}^{\text{I}} \text{NO}_2 + 5 \text{ Hg}^{\text{II}} (\text{NO}_2)_2 + 2 \text{ Ag}^{\text{I}}$<br>or $3 \text{ Hg}^{\text{I}} \text{NO}_2 + \text{H}_2 + \text{H}_2$<br>+ $2 \text{ Ag}^{\text{I}}$                                                                                          | 0.130                 | 0.973             | 0.257                                | 0.130                 |
| $10 \text{ Hg}^{\text{I}} \text{NO}_2 + 11 \text{ Hg}^{\text{II}} (\text{NO}_2)_2 + 7 \text{ Ag}^{\text{I}}$<br>or $7 \text{ Hg}^{\text{I}} \text{NO}_2 + 3 \text{ Ag}^{\text{I}}$<br>+ $5 \text{ Hg}^{\text{II}} (\text{NO}_2)_2 + 2$<br>+ $3 \text{ Ag}^{\text{I}}$                                    | 0.027                 | 0.034             | 0.274                                | 0.027                 |
| $18 \text{ Hg}^{\text{I}} \text{NO}_2 + 18 \text{ Hg}^{\text{II}} (\text{NO}_2)_2 + 5 \text{ Ag}^{\text{I}}$<br>or $3 \text{ Hg}^{\text{I}} \text{NO}_2 + \text{Ag}^{\text{I}}$<br>+ $2 \text{ Hg}^{\text{II}} (\text{NO}_2)_2 + \text{H}_2$<br>+ $4 \text{ Ag}^{\text{I}}$                              | 0.105                 | 0.031             | 0.614                                | 0.105                 |
| $6 \text{ Hg}^{\text{I}} \text{NO}_2 + 7 \text{ Hg}^{\text{II}} (\text{NO}_2)_2 + \text{Ag}^{\text{I}}$<br>or $2 \text{ Hg}^{\text{I}} \text{NO}_2 + \text{H}_2 + \text{H}_2$<br>+ $4 \text{ Ag}^{\text{I}}$                                                                                             | 0.057                 | 0.464             | 0.2284                               | 0.057                 |
| $15 \text{ Hg}^{\text{I}} \text{NO}_2 + 19 \text{ Hg}^{\text{II}} (\text{NO}_2)_2 + \text{Ag}^{\text{I}}$<br>or $2 \text{ Hg}^{\text{I}} \text{NO}_2 + \text{H}_2 + \text{H}_2$<br>+ $13 \text{ Hg}^{\text{II}} (\text{NO}_2)_2 + 20 \text{ Hg}^{\text{II}} (\text{NO}_2)_2$<br>+ $\text{Ag}^{\text{I}}$ | 0.26                  | 0.507             | 0.345                                | 0.26                  |
| $2 \text{ Hg}^{\text{I}} \text{NO}_2 + 3 \text{ Hg}^{\text{II}} (\text{NO}_2)_2 + \text{Na}^{\text{I}}$<br>or $2 \text{ Hg}^{\text{I}} \text{NO}_2 + \text{H}_2 + \text{H}_2$<br>+ $4 \text{ Hg}^{\text{II}} (\text{NO}_2)_2 + \text{Na}^{\text{I}}$<br>+ $\text{Ag}^{\text{I}}$                         | 0.081                 | 0.333             | 0.042                                | 0.081                 |
| $2 \text{ Hg}^{\text{I}} \text{NO}_2 + 2 \text{ Hg}^{\text{II}} (\text{NO}_2)_2 + \text{Na}^{\text{I}}$<br>or $2 \text{ Hg}^{\text{I}} \text{NO}_2 + \text{H}_2 + \text{H}_2$<br>+ $3 \text{ Hg}^{\text{II}} (\text{NO}_2)_2 + \text{Na}^{\text{I}}$<br>+ $\text{Ag}^{\text{I}}$                         | 0.34                  | 0.980             | 0.120                                | 0.34                  |

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ON MERCUROUS IODIDE—*A new Method of its Preparation.*

The yellow residue in the flask (see previous paper) consisting presumably of a mixture of mercurous iodide and the unacted-upon mercurous nitrite was well powdered and introduced into a combustion tube, plugged with asbestos and heated in a tube-heater (Röhren-Oefen.). The powder occupied nearly one-third the length of the tube. When the temperature rose to about 135° C, nitrous fumes began to be disengaged, and an oily liquid collected at the mouth of the tube. This liquid is nitro-ethane, a portion of which obstinately remains absorbed in the hard mass of the mixture referred to above.

On heating more than two hours from 155° to 163°, for the most part stationary at the latter temperature, a thin deposit of lustrous lemon-yellow scales was obtained. The yield however was very poor. Next day the heat was raised to 192°, and the temperature maintained nearly constant for three hours: a sublimate of a compact mass of yellow and orange-yellow crystals was the result.

In another experiment the sublimation was carried on between 190°–210° C. stationary for the most part at 210°, in this case orange-yellow crystals were obtained. In several experiments, however, conducted within the above range of temperatures, the sublimate which was deposited nearest the source of heat was of a dark brown tint; next to it was a deposit of orange-yellow and yellow tablets respectively; and, last of all, near the mouth of the tube was a ring of scarlet crystals of *mercuric* iodide. Sometimes it so happened that by far the larger proportion of the sublimate was of scarlet *mercuric* iodide; but whether this was due to the decomposition or dissociation of mercurous iodide formed at first ( $\text{Hg}_2\text{I}_2 = \text{HgI}_2 + \text{Hg}$ ) or not is not clear. More than a dozen experiments were carried on, and the experiences accruing therefrom are recorded above.

*General properties:*—In Yvon's\* experiment in which Mercurous Iodide was prepared by the direct union of the elements, only the yellow and orange-yellow crystals are described. According to this chemist sublimation begins at 190° C. My own experience confirms his in the main, though I have noticed that a small quantity of mercurous iodide almost always sublimes between 163° and 170° C.

The dark brown variety when powdered and kept in contact with dilute nitric acid turns dirty yellow, and the orange-yellow under similar conditions orange-red, without undergoing change in the composition; but boiled for some time with the dilute acid, both these varieties are gradually transformed into *mercuric* iodide, and from the

\* Compt. Rend. 76, p. 1607.

hot mother liquor also bright scarlet spangles of mercuric iodide crystallize out on cooling.

*Result of Analysis*:—Estimation of iodine. The methods described in the standard works of Fresenius, Crookes, &c., for the estimation of iodine in mercurous iodide appeared to be tedious and troublesome in view of the numerous determinations involved. Reduction was effected with zinc and sulphuric acid under certain modifications. The compound is finely powdered and transferred to a flask. Pure granulated zinc and dilute sulphuric acid are then added together with a few pieces of scrap platinum, when evolution of hydrogen at once sets up; the flask is kept actively rotated. After a few minutes the zinc becomes amalgamated and further action ceases. A drop of platonic chloride is now added, reduction proceeds, and a pink colour pervades the liquid, and the flask is shaken as before. When the reduction is complete the solution should be perfectly clear and colourless, and there should not be any trace of a powdery black residue at the bottom of the flask. The iodine is estimated in the usual way, and the additional halogen introduced with the standard  $\text{Pt.Cl}_4$  drop, corresponding in the present instances to 0.005  $\text{AgCl}$ , allowed for. Sometimes the zinc is treated beforehand with the dilute acid and a few drops of  $\text{PtCl}_4$ , and the *platinized* zinc, washed free from chlorine, is added in successive instalments to bring about reduction, which is finished in 20 min. to half an hour.

As control experiments, iodine in resublimed mercuric iodide was estimated according to the above method. Thus:

|       |                          |      |                                                                                                                                                                                                                                                                                                                   |   |    |       |       |
|-------|--------------------------|------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---|----|-------|-------|
|       | (1) 0.2232 g.            | gave | 0.2324 $\text{AgI}$                                                                                                                                                                                                                                                                                               |   |    |       |       |
|       | (2) 0.0604               | „ „  | 0.0625 „                                                                                                                                                                                                                                                                                                          |   |    |       |       |
|       | Calc. for $\text{HgI}_2$ |      | Found                                                                                                                                                                                                                                                                                                             |   |    |       |       |
| I:    | 55.95                    |      | <table style="margin-left: auto; margin-right: auto; border-top: 1px solid black; border-bottom: 1px solid black;"> <tr> <td style="padding: 0 10px;">I</td> <td style="padding: 0 10px;">II</td> </tr> <tr> <td style="text-align: center;">56.27</td> <td style="text-align: center;">56.00</td> </tr> </table> | I | II | 56.27 | 56.00 |
| I     | II                       |      |                                                                                                                                                                                                                                                                                                                   |   |    |       |       |
| 56.27 | 56.00                    |      |                                                                                                                                                                                                                                                                                                                   |   |    |       |       |

Result of analyses of the dark brown, orange-yellow and yellow modifications of mercurous iodide.

|     |            |            |                     |                |
|-----|------------|------------|---------------------|----------------|
| (1) | 0.4282 g.  | gave       | 0.3043 $\text{AgI}$ | whence I=38.40 |
| (2) | 0.2204 „ „ | 0.1577 „ „ | „ „                 | =38.67         |
| (3) | 0.2558 „ „ | 0.1834 „ „ | „ „                 | =38.74         |
| (4) | 0.2038 „ „ | 0.1446 „ „ | „ „                 | =38.34         |
| (5) | 0.0824 „ „ | 0.0587 „ „ | „ „                 | =38.47         |

Theory for  $\text{HgI}$  requires I=38.84%, the Mercury amounted to 61.24%, that demanded by theory being 61.16%.

It will much facilitate operation if between 0·2 to 0·15 g. be taken for purposes of analyses. In the case of the dark brown variety of the haloid it is advisable to examine it carefully with a magnifying glass as inside its thick crust minute globules of mercury are often found enclosed.

From the foregoing inquiry it is evident that when the residue in the flask after the interaction of mercurous nitrite and ethyl iodide is heated in a tube between 190°–210°, mercurous iodide sublimes off. The compact mass of crystalline tablets thus obtained varies in all gradations of tint from lemon-yellow and orange-yellow to orange-brown and even dark brown.

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XIX.—*Description of a new Himalayan genus of Orobanchaceæ.*—

By J. S. GAMBLE, M.A., F.R.S., and D. PRAIN.

[Received 7th August; Read 5th October, 1900.]

GLEADOVIA Gamble & Prain.

*Calyx* tubulosus, parum inflatus limbo æqualiter 5-lobo. *Corollæ* tubus parum incurvus, labium posticum incurvo-erectum concavum minopere emarginatum, anticum brevius suberectum lobis 3 subæqualibus erectis. *Stamina* inclusa filamentis apice in connectivum conicum dilatatis, antherarum loculi æquales adnati basi divergentes et mucronato-aristati. *Ovarii* placentæ 4, per paria approximatae, medioque confluentes; stigma dilatatum late æqualiter 2-lobum.—*Herba* parasitica carnosa rhizomate incrassato, squamis ovatis suffulta. *Flores* densius paniculati, pedicellati, 2-bracteolati. *Color* pallide purpurea.—*Species* singula, Himalaica.

The interesting plant for which we propose the above generic description was discovered in Jaunsar in 1898 by the officers of the Imperial Forest School, Dehra Dun; we dedicate it to Mr. F. Gleadow, who was the first actually to find it.

Our plant has all the facies of a *Christisonia*, but cannot be referred to that genus because both anther-cells are perfect, because the corolla is very markedly 2-labiate in place of being sub-equally 5-lobed, and because the two stigmatic lobes are equally large.

The nearest ally of our plant seems to be the American genus *Conopholis* Wallr., with which it agrees as regards corolla and, except that they are not exserted, as regards stamens, but from which it differs in having an equally 5-lobed calyx and a 2-lobed stigma. From